REMARKS

Applicants respectfully request reconsideration of the present application in view of the foregoing amendments and in view of the reasons that follow. The amendment to claim 1 is supported by page 7, lines 15-20 and Examples 1-3 on page 9 of the specification.

Rejections Under 35 USC 102(b)

Applicants traverse the rejections under 35USC 102(b) for the following reasons.

Hayden (US 5,387,751)

The catalyst used in Hayden is a silver catalyst supported on α-alunima, which was calcined before use (see at lines 7 to 11, col. 3, and lines 52 to 53, col. 6). Hayden teaches that the catalyst is dried before use. The process of Hayden is silent on the utilization of water vapor in the epoxidation process. See the Examples.

In Example 17, a process gas stream containing 30% propylene, 8% oxygen and 1150 ppm dichlroromethane was used and the reaction was performed with oxygen selectivity/conv. of 14%/12% and 35%/6% as shown in Table 6, col. 13. The amount of oxygen that was used for undesirable side reactions other than epoxydation reaction is calculated to be less than 1%. Then the amount of water that may have resulted from such oxygen per mol of propylene in the process gas stream, or in the reaction would be far less than the recited amount in the present claim.

The Examiner mentions the chlorine-containing reaction modifier such as a Cl-C10 compound. However, it is stated that the concentration of such compound should be in the range of 0.1 to 500 parts per million parts of the reaction medium by weight. The amount of the modifier is too much small to render the presently claimed amount of water anticipated.

Hayden does not teach or disclose the amount of water that was added to the reaction in the presently claimed process either explicitly or inherently.

Boeck (US 5,618,954)

The process of Boeck is directed to epoxidation of butadiene using a catalyst containing Ag supported on α-alunima (penultimate paragraph col. 7). Boeck is silent on propylene and therefore cannot anticipate the present claims.

Nakashiro (US 6,498,122)

The process of Nakashiro is directed to the epoxidation of ethylene. Nakashiro is silent on propylene. Superheated steam is applied to the impregnated carrier to make the distribution of silver and alkali metal supported in the resulting catalyst uniform as described at lines 46 to 49, col. 4. But the production of ethylene oxide is not conducted in the presence of such superheated steam.

In connection with Boeck and Nakashiro, the applicants attach hereto as Appendix I Applied Catalysis A: General 221 (2001) 73-91 by Monnier. Monnier discloses under 3.2. Epoxidation of 1,3-butadiene, from the last paragraph on page 82 to line 5, on the right column, p.83, in Table 2 that Ag catalyst in which Ag is supported on α-alumina shows catalytic activity for oxidation of butadiene and ethylene having vinyl hydrogens only but is not suitable to epoxidize propylene and butene having allyl hydrogen atoms. In the disclosed reactions, ethylene and butadiene were converted to corresponding epoxy compounds. Propylene and butene, however, were not effectively converted to corresponding epoxy compounds.

Monnier teaches that the Ag catalyst in which Ag is supported on α-alumina, which were also disclosed as preferable or typical catalyst in Hayden, Boeck, and Nakashiro, did not show similar effect to propylene though the differences between propylene and ethylene or butadiene is just one carbon atom and the nature of hydrogens. It can be said from the teachings of these references that in the real epoxidation reactions propylene behaves rather in a different manner than ethylene or butadiene.

Therefore, the teachings of Boeck or Nakashiro cannot anticipate the presently claimed invention.

Mul (US 6,392,066)

Mul discloses the epoxidation catalyst and epoxydation reaction of ethylene, and that in the penultimate paragraph col. 7 that the feedstream may contain inert gas such as nitrogen or helium as a ballast or diluent, and mentions that carbon dioxide is not desirable in view of selectivity and should preferably be removed from the feedstream.

Water vapor is referred to in the same context in which carbon dioxide is not considered a desirable component and is to be removed.

Although during the catalyst preparation a water solution is employed it is described at the last two lines of Example 1, col. 8, that the prepared catalyst is calcined at 375°C before use.

In addition there is no mention of the addition or the effect of water vapor in the oxidation reaction as it can be seen from the descriptions (e.g. Example 5, col. 9).

The process of Mul is silent on the use of water in the epoxidation process per se and therefore, cannot anticipate the present invention.

Conclusion

Applicants believe that the present application is now in condition for allowance. Favorable reconsideration of the application as amended is respectfully requested. The Examiner is invited to contact the undersigned by telephone if it is felt that a telephone interview would advance the prosecution of the present application.

The Commissioner is hereby authorized to charge any additional fees which may be required regarding this application under 37 C.F.R. §§ 1.16-1.17, or credit any overpayment, to Deposit Account No. 19-0741. Should no proper payment be enclosed herewith, as by a check or credit card payment form being in the wrong amount, unsigned, post-dated, otherwise improper or informal or even entirely missing, the Commissioner is authorized to charge the unpaid amount to Deposit Account No. 19-0741. If any extensions of time are needed for timely acceptance of papers submitted herewith, Applicant hereby petitions for such extension under 37 C.F.R. §1.136 and authorizes payment of any such extensions fees to Deposit Account No. 19-0741.

Respectfully submitted,

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Applied Catalysis A: General 221 (2001) 73–91

APPLIED CATALYSIS A: GENERAL

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The direct epoxidation of higher olefins using molecular oxygen

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Abstract

Recent developments in olefin epoxidation have shown promising results indicating that higher olefins can be directly epoxidized using molecular oxygen, or indirectly, by using molecular oxygen to generate an active and selective oxidant in situ during reaction. Indirect approaches have utilized bifunctional catalysts that combine new catalyst components that generate such oxidants as H_2O_2 in situ with the functional component that activates H_2O_2 for olefin epoxidation. This approach is currently limited by the low rates of in situ generation of H_2O_2 and subsequent low rates of olefin epoxide formation. Heavily-modified, silver catalysts have also shown promise as catalysts for propylene epoxidation. These catalysts contain much higher silver and alkali and alkaline earth metal loadings than their analogs used for ethylene epoxidation and are quite different in terms of their chemical and physical properties. Currently, these compositions exhibit activities and selectivities to propylene oxide that are too low for commercial application, although further research and development may further improve catalyst performance.

Silver-based catalysts have also been used to epoxidize a wide variety of higher olefins, such as 1,3-butadiene, that do not contain allylic hydrogen atoms, or higher olefins that contain non-reactive allylic hydrogen atoms, such as norbornene. Silver-based catalysts used for selective epoxidation of non-allylic, or kinetically-hindered, olefins require promoters, typically cesium, rubidium, or thallium salts, to assist in the desorption of the olefin epoxide. Such catalysts are extremely active, selective, and stable under extended reaction conditions.

Keywords: Epoxidation; Silver; Molecular oxygen; Hydrogen peroxide; Titanium dioxide; Titanium silicalite; Propylene; Butadiene; Promoters; Gold; Palladium; Alkali promoters

1. Introduction

The epoxidation of olefins is an extremely important class of catalytic reaction in the chemical industry. The silver-catalyzed, gas phase epoxidation of ethylene using molecular oxygen is one of the most successful examples of heterogeneous catalysis to date. In 1998, the domestic production of ethylene oxide alone was 8.14 billion lbs [1]. In spite of the versatility and importance of olefin epoxides in the chemical processing industry, until very recently, no other olefins had been commercially epoxidized using only molecular oxygen as the oxidant. In early 1997, Eastman Chemical Company began production of 3,4-epoxy-1-butene (EpB), the product from mono-epoxidation of 1,3-butadiene, at the semiworks scale of production [2,3]. Efforts to directly epoxidize other higher olefins, such as propylene, to their corresponding epoxides using molecular oxygen in a commercially-viable process have not been as successful. Many explanations have been proposed for the failure to directly epoxidize allylic olefins, such as propylene, to their corresponding epoxides, although the most obvious reason is the reactivity of allylic C–H bonds. The bond dissociation energy of the allylic C–H bond in propylene is 77 kcal/mol, while the vinylic C–H bond strength in ethylene is

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0926-860X/01/$ – see front matter
PII: S0926-860X(01)00799-2

112 kcal/mol [4,5]. Thus, electrophilic attack by oxygen and abstraction of one of the allylic C–H bonds in propylene becomes energetically more favorable than electrophilic addition of oxygen across the C=C double bond. Once abstraction of hydrogen occurs, epoxide formation is precluded.

However, higher olefins are successfully epoxidized using indirect oxidation routes, such as the well-known peroxidation process for propylene epoxidation, whereby organic hydroperoxides or organic peracids are reacted with propylene to produce equimolar amounts of propylene oxide and organic alcohols and organic acids, respectively. For instance, the hydroperoxidation process of propylene by *tert*-butyl hydroperoxide or ethylbenzene hydroperoxide is typically conducted in the liquid phase in the presence of high-valent, homogeneous Mo, V, or Ti catalysts at 90–150 °C and 15–65 bar pressure to produce propylene oxide along with *tert*-butyl alcohol or ethylbenzene [6]. The *tert*-butyl hydroperoxide or ethylbenzene hydroperoxide oxidants are formed ex situ in a separate step from isobutane and ethylbenzene. This technology, which is well established and provides much of the commercially-produced propylene oxide, suffers from the fact that the co-products formed during reaction are actually produced in a greater weight fraction than propylene oxide. Thus, successful application of this technology requires utilization of the by-product stream. Similarly, use of peracetic acid to oxidize propylene to propylene oxide [4] requires an outlet for the acetic acid by-product. It also needs an inexpensive source of acetaldehyde which is oxidized to form the peracetic acid.

The discovery of the titanium silicalite TS-1 by Taramasso et al. [7] opened a new pathway for the epoxidation of higher olefins by permitting the use of hydrogen peroxide (H_2O_2) as the indirect oxidant to epoxidize allylic olefins and to form only H_2O as an environmentally-friendly by-product [8,9]. This process is very selective to epoxides such as propylene oxides with selectivities >95%, based on propylene, and 70–99% based on H_2O_2. However, because of the relatively high cost of H_2O_2, this process has not been commercialized to date on a large scale.

Consequently, most current research and development has focused on either the use of molecular O_2 as the direct oxidant for selective epoxidation or on in situ generation of indirect oxidants, such as H_2O_2, which also employs molecular O_2 and generates only H_2O as the by-product. Quite simply, it is recognized that the least expensive oxidant for producing epoxides is molecular oxygen and that capital expenses required to construct commercial manufacturing facilities are typically lower for those processes that use molecular O_2. Thus, in this report, we will discuss those catalysts and processes that either use molecular oxygen as the direct oxidant or involve O_2 to form in situ oxidants to produce higher olefin epoxides. The silver-catalyzed epoxidation of ethylene using O_2 will not be discussed in this report, except to provide reference for those examples that also use silver catalysts for the epoxidation of higher olefins.

2. Epoxidation by in situ generation of oxidant using O_2

2.1. *Epoxidation using transition metal complexes*

Most of the earlier efforts using molecular oxygen as the in situ oxidant for higher olefin epoxidation have been conducted in the liquid phase using soluble metal complexes as homogeneous catalysts. Selected examples of these catalysts and performance are summarized in Table 1. Examples that require the use of non-olefin reactants, such as aldehydes, that themselves undergo oxidation, are not included, since those examples are the same as epoxidation using peracids. In those examples cited in Table 1, most of the mechanistic schemes involve epoxidation by free radical processes involving peroxides and hydroperoxides in solution. Thus, the overall performance is the sum of both a catalytic as well as a thermal, free radical component, making it difficult to determine the efficacy of the homogeneous catalyst. For instance, Budnik and Kochi [10] reported that when Co(III) acetylacetonate was used as the catalyst during the epoxidation of norbornene and *tert*-butyl ethylene, the epoxidation reactions showed induction periods characteristic of radical chain processes, in this case β-peroxyalkyl radicals. In these cases, the primary mechanism for olefin epoxide formation is not catalytic, but is thermal autoxidation. As is typical of most reactions proceeding by free radical mechanisms, selectivities to the olefin epoxides are often unacceptably low and the number of different products too large to make

Table 1
Epoxidation of olefins using homogeneous catalysts

Catalyst	Reaction conditions			Reaction time (h)	Olefin	Conversion of olefin (%)	Selectivity to epoxide (%)	Mechanistic features	Reference
	Temperature (°C)	Pressure (psig)	Solvent						
Co(III) acetylacetonate	60–130	150	Benzene	18	Norbornene	95	43	Co(III)-initiated, radical chain reaction	[10]
Ag(I) oxo clusters	150	650	Benzene	Not given	Propylene	7.5	32–65	Ag(II) oxo-initiated radical chain reaction	[11]
Ni(II) acetylacetonate	100	30	Mesitylene and butanol	6	Substituted norbornene	100	59–65	Ni(II)-catalyzed formation of alcohol–O_2 complex to epoxidize olefin	[12]
Cu(I) porous oligomer	25	150	Propionitrile	24	Propylene	0.1	50	Direct epoxidation by –(O–Cu(I)–O–O–)$_n$ chain	[13]
Pt(II) halide	100	600	Acetonitrile	14	Propylene	1.6	23	Not stated	[14]
$EuCl_3$ + Zn powder	40	15	CH_2Cl_2 and CH_3COOH	1	1-Hexene	3.2	66	Not stated	[15]

separation economically viable. For those examples employing soluble Cu(I) and Pt(II) complexes as catalysts, however, no free radical process was operative in either case. However, both C_3H_6 conversions and propylene oxide selectivities were unacceptably low in both instances, typical for catalytic, olefin epoxidation reactions using soluble, transition metal complexes. Similarly, the complex system employing $EuCl_3$, Zn powder, and CH_3COOH as catalyst components results in 1-hexene epoxide formation at a turn over frequency of 13.8 h^{-1}. Clearly, the data reported in Table 1 indicate the problems often cited for the use of liquid phase, olefin epoxidation reactions. The catalytic reactions are slow, giving unacceptable rates of epoxide formation; further, it is difficult to suppress free radical, chain reactions from occurring in solution. While radical reactions are much faster, they are inherently non-selective, leading to poor utilization of olefin feedstock and expensive separation processes to isolate the desired epoxide product. A much more complete discussion of transition metal complexes as olefin epoxidation catalysts has been compiled in an excellent review by Jørgensen [16].

2.2. Epoxidation using molten salts

A very different method for propylene epoxidation has been reported by workers at Olin Corporation [17,18]. Molten salt mixtures, with $LiNO_3$, $NaNO_3$, and KNO_3 being the preferred alkali metal nitrate salts, were used to assist in the epoxidation of a vapor phase feed consisting of propylene, oxygen and nitrogen at temperatures ranging from 180 to 400 °C. While the specific nature of the catalytic activity of the molten salts is not specified nor has it been confirmed, it is believed that propylene oxide is primarily formed by the thermal reaction of propylene with oxygen, and the primary role of the molten salts is to function as a high capacity, heat removal medium, which essentially maintains an isothermal temperature profile during the highly exothermic, selective and non-selective oxidation reactions. The reaction products, which are gas stripped from the molten salt bed, are primarily composed of propylene oxide, acrolein, allyl alcohol, and acetone as well as CO and CO_2. For example, using a molten bed composition of 30 mol% $LiNO_3$, 20 mol% $NaNO_3$, and 50 mol% KNO_3 at a reaction temperature of 225 °C and 358 psig pressure, a feedstream consisting of 53% C_3H_6, 8% O_2, and balance N_2 (total flow = 2000 cm^3/min (STP)) was partially converted to 57% propylene oxide, 7% other C_3-oxygenates, and balance CO/CO_2; conversion of C_3H_6 was 9.7%. It is difficult to infer the nature of the catalyst formed by the mixture of the molten salts, although the selectivity to PO does seem higher than normal for a purely thermal, even isothermal, oxidation reaction. The reaction is run lean in molecular O_2, which does suggest that the reaction may be largely thermal in nature, and that selectivity is controlled by restricting O_2 concentration in the feed. Another supporting reason that the mixed molten salts may not function as true catalysis is the basis of another patent published from Olin Corporation [19]. In this patent, Meyer claims that aldehydes, including acrolein, acetaldehyde, and propionaldehyde, which are normally isolated in small amounts during operation of the molten bed process, may be utilized in a second reactor to effect the co-oxidation of unreacted C_3H_6 with the peracids formed by the thermal reaction of these aldehydes and O_2. Additional propylene oxide is then formed by the well-known epoxidation by peracids, which has been mentioned above. Thus, it is now difficult to determine how much of the propylene oxide which is produced in the molten salt medium is actually formed from some unspecified catalytic reaction using molten salts and how much propylene oxide is produced from the co-oxidation of C_3H_6 by peracids, which would be formed in situ in the molten medium. Again, we have a situation, where it is difficult to determine whether higher olefins have been directly epoxidized by molecular O_2, or whether another variant of co-oxidation by hydroperoxides or peracids have occurred yet again.

2.3. Gas phase epoxidation using bifunctional, heterogeneous catalysis

2.3.1. Palladium supported on TS-1 supports

One of the most current and promising areas of higher olefin epoxidation, which circumvents many of the uncertainties and difficulties mentioned above, involves the use of novel, bifunctional heterogeneous catalysts which apparently function by generation of in situ H_2O_2 from H_2 and O_2. The metallic component, which is believed to generate H_2O_2, is typically supported on TiO_2, which contains Ti^{n+} sites, which

activate the H_2O_2 for electrophilic addition to the C=C double bond of the substrate olefin. Hölderich and coworkers [20,21] have reported that propylene oxide can be produced using a bifunctional, heterogeneous catalyst composed of palladium supported on titanium silicalite (TS-1), or more preferably, platinum-promoted, palladium supported on TS-1. The reaction, which is run as a liquid phase slurry reaction typically uses a mixture of methanol and water as the slurry liquid. This bifunctional composition uses Pd, or Pt-promoted Pd to generate H_2O_2 from the H_2 and O_2 which are present, along with propylene, in the feed. Once formed, the H_2O_2 is activated by the appropriate Ti^{n+} sites on TS-1 support. Reaction of propylene with the activated hydroperoxide species then forms propylene oxide. The obvious benefits of this catalyst system and feed composition is that expensive H_2O_2 is not required as the source of the hydroperoxide species, which is the oxidant for TS-1. Hölderich has examined the effects of different oxidants (H_2O_2 versus H_2 and O_2) and catalyst compositions (TS-1 and Pt-Pd/TS-1) for the production of propylene oxide. Key results, taken from [21] are shown below in Table 2. The Pt-Pd/TS-1 catalyst was made using wet impregnation of an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ and $Pd(NH_3)_4(NO_3)_2$ to give a composition of 0.1 wt.% Pt-1.0 wt.% Pd supported on TS-1. The catalyst precursor was then thermally reduced (by the NH_3 ligands) by heating at 150 °C for 1 h in flowing N_2. An autoclave charged with 0.2 g_{cat} and 15 g CH_3OH and 5 g H_2O was sealed and 10 g C_3H_6 (0.24 mol) and 7 bar H_2 (59 mmol), 10 bar O_2 (92 mmol), and 15 bar N_2 were used to pressure the reactor up to reaction conditions. When H_2O_2 was used as the oxidant, 8 g of 30% H_2O_2 were used in place of H_2 and O_2.

Table 2
Epoxidation of propylene

Oxidant	Catalyst	PO yield (%) (based on C_3H_6 conversion and PO formed)
H_2O_2	TS-1	39.3
H_2O_2	0.1 wt.% Pt-1.0 wt.% Pd/TS-1	21.3
$H_2 + O_2$	TS-1	0
$H_2 + O_2$	0.1 wt.% Pt-1.0 wt.% Pd/TS-1	5.3

The results show that the use of H_2O_2 as oxidant and TS-1 as catalyst is the best combination of oxidant and catalyst. The lower yield when H_2O_2 is used with the Pt-Pd/TS-1 catalyst is due to the decomposition of some of the H_2O_2 by the Pt-Pd part of the catalyst before it reacts with C_3H_6. The use of $H_2 + O_2$ as the oxidant indicates that Pt-Pd is required for H_2O_2 formation. The lower yield for propylene oxide using $H_2 + O_2$ (5.3%) rather than H_2O_2 (21.3%) suggests that formation of H_2O_2 is rate limiting for propylene oxide formation.

In addition to the limitations of Pt-Pd/TS-1 to form H_2O_2 at rates sufficient to have higher yields of propylene oxide, the simultaneous addition of H_2 and C_3H_6 and H_2 and O_2 in the presence of noble metals such as Pt and Pd leads to severe yield losses by formation of C_3H_8 and H_2O, respectively. Hölderich has found that key to controlling reaction pathways to produce H_2O_2 and, subsequently, propylene oxide is that the Pd crystallites must be highly dispersed and preferentially exist as small, needle-shaped aggregates, rather than the more typical large, spherical-shaped particles. Calcination and reduction procedures for the impregnated $Pt(NH_3)_4(NO_3)_2$ and $Pd(NH_3)_4(NO_3)_2$ salts were critical in determining the final shape (needle versus spherical), size, and surface oxidation state (Pd^0 versus Pd^{2+}) of the final Pd crystallites. Not unexpectedly, milder calcination (lower temperatures and lower O_2 concentrations) and reduction (lower temperatures and lower H_2 concentrations) conditions favored the formation of small, needle-shaped Pd aggregates that contained the largest fraction of surface Pd^{2+} sites. Because the concentration of surface sites correlated well with the formation rates of H_2O_2, the surface concentration of Pd^{2+} was viewed as critical in determining maximum activity for the formation of propylene oxide. The addition of minor amounts of Pt to Pd/TS-1 dramatically increased the concentration of Pd^{2+} relative to Pd^0. For 1 wt.% Pd/TS-1 the addition of 0.01 and 0.02 wt.% Pt increased the surface concentration of Pd^{2+} from 12% (no Pt) to 43 and 56%, respectively. Further increases in the amount of Pt up to 1.0% to give 1/1 weight ratios of Pt/Pd did not change the surface concentration of Pd^{2+}, but did change the shape of the Pd aggregates from primarily rod-shaped to a mixture of rod-shaped crystallites and the undesirable, spherical crystallites. Thus, the optimum level of Pt is a balance of increasing the

desirable surface concentration of Pd^{2+} with undesirable changes in the surface morphology of the Pd aggregates from needle-shaped to spherical. Further, since supported Pt catalysts are very active for the hydrogenation of C_3H_6 to C_3H_8, excess loadings of Pt must be avoided.

Little attention has been directed to determining the site for C_3H_6 interaction with the H_2O_2-activated surface. It is not clear whether there is direct interaction of gas phase C_3H_6 with the Ti–O–O–H site, or whether C_3H_6 is chemisorbed on the Pd or Pt surface adjacent to the H_2O_2-covered Ti^{n+} site. The latter possibility would suggest that propylene oxide formation occurs at the Pd (or Pt-Pd)–Ti^{n+} interface, such as at the edges of the needle-shaped, palladium aggregates in contact with the TS-1 surface. If this is the case, the concentration of active, bifunctional sites will be quite limited, restricting the maximum rate of propylene oxide formation. The performance of this type of catalyst indicates the difficulty in forming a bifunctional catalyst having the correct composition, morphology, and distribution of active sites to give active and selective formation of propylene oxide. Failure to maintain the proper balance of Pd^{2+} sites, Pd morphology, and concentration of Pt promoter results in a catalyst having both low activity and low selectivity. Regardless, the concept of combining the site for formation of the oxidant (H_2O_2) with the site for olefin epoxidation is a positive step in the direction to produce propylene oxide and other higher olefins directly from O_2.

Clerici and Ingallina [22] have reported that in situ H_2O_2 generation can be accomplished using an alkylated anthraquinone as the oxygen carrier for H_2O_2 generation, rather than H_2 as the oxygen carrier. This modification is based on the current, commercial method for stand-alone H_2O_2 generation using anthraquinone, which involves the steps of hydrogenation of anthraquinone to hydroanthraquinone followed by oxidation with O_2 to liberate H_2O_2 and regenerate anthraquinone. Clerici argues that the selection of TS-1 as the epoxidation catalyst, rather than TiO_2, permits the use of the zeolitic pores and channels in TS-1 to exclude diffusion of any of the anthraquinone species into the interior of TS-1, where the epoxidation takes place between H_2O_2 and the olefin. Thus, catalyst lifetime should be extended and non-selective degradation of anthraquinone species should be minimized. Clerici reports that C_3H_6 is selectively epoxidized to propylene oxide at 78% yield at 30 °C and 1.5 h. reaction time using a solution containing ethyl hydroanthraquinone, O_2, C_3H_6, and TS-1 catalyst in methylnapthalene/CH_3OH solvent. However, this is not true in situ epoxidation, since the hydrogenation of ethyl anthraquinone by H_2 and Pd/C to form ethyl hydroanthraquinone was conducted ex situ. Thus, it is not clear how the addition of H_2 and Pd/C to the epoxidation reactor would affect overall performance of this process, although it is highly likely that hydrogenation of C_3H_6 and reduction of O_2 to form C_3H_8 and H_2O, respectively, would adversely affect selectivity and activity for propylene oxide formation.

2.3.2. *Epoxidation using Au supported on TiO_2*

Very intriguing work recently reported by Haruta and coworkers [23–26] have demonstrated that a feedstream consisting of C_3H_6, O_2, and H_2 can be selectively epoxidized to form propylene oxide using highly dispersed gold supported on TiO_2. Although gold has historically been regarded as being inactive for most catalytic reactions of interest, highly dispersed gold catalysts have been found to have exceptionally high activity for many types of oxidation reactions. In earlier work, Haruta et al. [27] found that highly dispersed gold catalysts were active for CO oxidation at temperatures as low as −50 °C. These results, which were reproduced by others [28], prefaced the discovery that C_3H_6 could be selectively epoxidized to propylene oxide using $H_2 + O_2$ as the selective oxidant. For a much more complete survey of various reactions catalyzed by supported gold catalysts, see the excellent review by Bond [29].

Haruta has found that that selective epoxidation of C_3H_6 occurs for gold particles supported on TiO_2 when the Au particles exist as hemispherically-shaped particles preferably between 2.0 and 4.0 nm in diameter. For example, vapor phase epoxidation using 0.50 g of 0.98 wt.% Au/TiO_2 at 50 °C in a gas mixture of $C_3H_6/O_2/H_2/Ar$ = 10:10:10:70 at a total flow of 33.3 cm^3/min gave 99% selectivity to propylene oxide; however, conversion of C_3H_6 was only 1.1%. Conversion of H_2 was 3.2%, indicating much of the H_2 was oxidized to H_2O, not H_2O_2. Increasing the temperature to 80 °C resulted in preferential combustion of H_2 and C_3H_6 to H_2O and H_2O/CO_2, respectively. Thus, selective operability is limited to an upper temperature of approximately 50 °C.

Catalysts containing gold particles <2 nm diameter primarily formed C_3H_8 from the selective hydrogenation of C_3H_6. Catalyst containing gold particles >4 nm in diameter were still selective for propylene oxide formation; however, the rate of formation, based on Au loading, decreased due to lower concentration of active Au sites as particle size increased. Formation of small, supported Au particles is accomplished by a deposition–precipitation technique, rather than the usual method of wet impregnation of a soluble gold salt, followed by calcination/reduction. Gold is deposited on the TiO_2 surface by precipitation of $Au(OH)_3$ from a basic solution of chloroauric acid at pH = 7–10, onto the TiO_2 support. After washing to remove the residual Cl^-, the catalyst was calcined at 400 °C to form the gold particles. Only by using the deposition–precipitation technique could hemispherical Au particles with diameters between 2.0 and 4.0 nm be prepared.

Clerici and Ingallina [22] has proposed the following mechanistic scheme in Fig. 1 to explain the features of these gold catalysts for the epoxidation of C_3H_6.

In this scheme, O_2 is inserted into a bridged Ti^{4+}–Au^+ site to form an activated molecular oxygen species. Reaction with H_2 forms the hydroperoxo species, which after elimination of H_2O, gives the bridging peroxo moiety. Presumably, this is the active oxygen species that reacts with C_3H_6 to form propylene oxide, although the bridging hydroperoxo species could also selectively react with C_3H_6 to form propylene oxide. The site for C_3H_6 adsorption is not obvious in the above scheme, although it is believed that C_3H_6 is adsorbed and that adsorption occurs on unspecified Au sites. Earlier work by Kasai [30] using ESR methods has shown that C_3H_6 is chemisorbed on non-oxygen covered, Au surfaces through the interaction of the π-bond of C_3H_6 with an sp_y band of a gold surface atom. Interestingly, Kasai found that neither C_2H_4 nor C_3H_6 chemisorbed on clean Ag surfaces; pre-adsorption of oxygen on Ag was necessary for olefin adsorption to occur, in agreement with many studies involving the adsorption of olefins on Ag surfaces, e.g. ethylene on Ag(1 1 1) surfaces [31], 1-butene on Ag(1 1 0) surfaces [32], and 1,3-butadiene on Ag(1 1 0) surfaces [33].

The proposed role of the Ti^{4+}–Au^+ site in the above mechanism implies that propylene oxide formation occurs at the interfacial edge of the hemispherical Au particles and the TiO_2 support. This is consistent with the recent results of Nijhuis et al. [34], who compared the catalytic activities of gold dispersed on TiO_2 and TS-1 supports. The authors found that for similar gold weight loadings and crystallite sizes the activity of the supported TiO_2 catalyst was greater than that of the TS-1 catalyst. They concluded that the interfacial contact of the Au particles with TiO_2 resulted in the formation of more Ti^{4+}–Au^+ sites than when TS-1 was the support, since the Ti content and surface concentration of Ti^{4+} sites is higher for TiO_2 than for TS-1. The authors also concluded that one of the primary causes for the generally observed low propylene oxide yields and deactivation of Au/TiO_2 catalysts with increasing time on-line (catalyst deactivation also

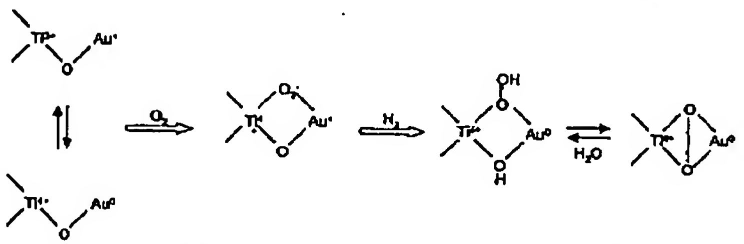


Fig. 1. Probable mechanism for the formation of the active oxygen species on Au/TiO_2 catalyst.

observed in Clerici and Ingallina's [22] work) is the strong adsorption of propylene oxide on the catalyst. The desorption of strongly-bound olefin epoxide products and the subsequent effects on catalyst design will be discussed in more detail when the epoxidation of higher olefins, such as 1,3-butadiene, over supported silver catalysts is discussed.

It is possible to calculate the upper limit of catalytically-active sites for supported Au/TiO_2 catalysts. The 0.98 wt.% Au/TiO_2 catalyst evaluated and characterized by Clerici and Ingallina [22] contained Au particles with a mean diameter (measured by transmission electron microscopy) of 2.4 nm. Using the solid state parameters from Anderson [35], we can calculate the dispersion of 2.4 nm Au particles to be 0.49. However, if only the interfacial Au sites on the perimeter of the hemispherical Au particles are active (since the active site is postulated to be a bridged Ti^{4+}–Au^+ species), then the effective dispersion of the Au particles decreases to 0.11. This gives an upper limit of the concentration of active sites, since not all the Au sites on the interfacial perimeter of Au and TiO_2 will be coordinated to Ti^{4+} sites. The propylene oxide formation rate reported by Haruta was 0.20 mmol/(h g_{cat}), corresponding to 3.34×10^{16} PO molecules/(s g_{cat}). The above catalyst contained a maximum of 3.2×10^{18} Au sites/g_{cat}, resulting in a turn over frequency for propylene oxide formation = 0.01 s^{-1}. Turnover frequencies in this range are approximately 20–100 times lower than reported turnover frequencies reported for ethylene oxide and epoxybutene formation and indicate one of the principal shortcomings of this catalyst system. Both C_3H_6 conversion and space time yields of propylene oxide must be dramatically improved for this system to become commercially-viable. Other problems include catalyst deactivation, which may be partially due to yet another problem with supported Au catalysts, that of preventing particle sintering under reaction conditions.

Regardless, the potential of this route has reaction has attracted the attention of a number of chemical companies and patents have recently appeared claiming selective production of propylene oxide using gold supported on various Ti-containing supports [36–42]. Most of these patents are concerned with proprietary advances that claim higher space time yields of propylene oxide and longer catalyst lifetimes under reaction conditions. For example, Bowman and coworkers [40–42] have reported that supported Au/TS-1 catalyst systems can be used to epoxidize C_3H_6 at 85% selectivity and 0.45% conversion of C_3H_6 with a GHSV of 1800 h^{-1}. The higher levels of C_3H_6 conversion are attained by operation at 165 °C. However, at these conditions, catalyst lifetime is limited, requiring frequent re-generations by calcination at high temperatures in air. Likewise, conversion of H_2 is high, with excess generation of H_2O. For the above reaction conditions, the molar H_2O/propylene oxide ratio varied between 13 and 18, indicating that most of the H_2 was oxidized to H_2O rather than H_2O_2.

3. Epoxidation using molecular oxygen

With few exceptions, all direct epoxidation reactions using O_2 as the oxidant are heterogeneous, silver-based catalysts that are promoted to greater or lesser extent with alkali and/or alkaline earth promoter salts. Chlorine is also used as a reaction moderator, and the chlorine may be added either during preparation, or added during reaction conditions by decomposition of organic chlorides in the feedstream. Because of the importance and current volume of propylene oxide, almost all effort has focused on selective epoxidation of propylene. The recent demonstration that olefins larger than propylene, such as 1,3-butadiene, styrene, and norbornene, can also be epoxidized has shifted some attention toward these potentially-important reactions and chemical intermediates. The following discussion will first discuss the development and state of the art for propylene epoxidation, before the discussion of higher olefin epoxidation.

3.1. *Epoxidation of propylene*

Although promoted silver catalysts normally used for ethylene epoxidation are virtually non-selective for propylene oxide formation due to the high reactivity of the allylic C–H bonds [43], a number of research efforts have shown that heavily-modified silver catalysts do show improved selectivity to propylene oxide. Compared to silver catalyst compositions used for ethylene oxide formation, these catalysts have much higher silver, alkali metal, alkaline earth, and chlorine loadings and, thus, are quite different in terms of

their physical and chemical properties. In some compositions, the modified silver composition is even unsupported. During preparation, the components of the catalyst are mixed into a liquid slurry, rather than being deposited using wet impregnation or incipient wetness methods onto a support, and then ball-milled to ensure even mixing and distribution of components before drying and calcination. The earliest work was reported by Kolombos and McCain [44] for a series of catalysts that were prepared by slurring silver powder with various group IIA metal halides, specifically $MgCl_2$, $CaCl_2$, and $BaCl_2$, which after drying gave compositions containing between 93 and 98 wt.% silver, with the balance being a group IIA metal chloride. Evaluation of these catalysts at 240–290 °C in a gas stream of 3% C_3H_6, 20–40% O_2, balance He gave selectivities to propylene oxide of 12–16% at propylene conversions between 80 and 90%. While these results were clearly marginal, they were much better than propylene oxide selectivities for silver catalyst compositions used for ethylene oxide production.

Later work by Thorsteinson [45] extended the study of heavily-modified, silver catalysts. A catalyst composed of 40 wt.% Ag and 1.5 wt.% K supported on or mixed with $CaCO_3$ (which itself can be considered to be a promoter as well as a support) was exposed to a feedstream of 10% C_3H_6, 9% O_2, 200 ppm C_2H_5Cl, and balance N_2 at 245 °C. Propylene conversion was 34% at a selectivity to propylene oxide of 47%.

Likewise, Bowman [46] prepared and evaluated a series of catalysts, characterized by having high weight loadings of Ag (approximately 60 wt.% Ag) and promoted with high, but unspecified, loadings of group IIA salts and supported on sodium silicate. Among the different catalysts, performance of a Mg-promoted catalyst at 180 °C in a flow stream of 68% C_3H_6, 29% O_2, and 3% H_2O vapor at a gas hourly space velocity (GHSV) = 200 h^{-1} gave a selectivity to propylene oxide = 47% at 3.7% C_3H_6 conversion. However, the low GHSV needed to attain 3.7% conversion underscores the low activity of this catalyst system.

The intrinsically low activity of these types of catalyst systems has been addressed by Lu and Zuo [47] for an unsupported Ag catalyst promoted with NaCl or $BaCl_2$. Reaction temperatures as high as 390 °C at a GHSV of 24,000 h^{-1} for a gas stream of 5% C_3H_6, balance air resulted in conversion of 54% of C_3H_6 at 26% selectivity to propylene oxide. Even at these short contact times, the selectivity is unusually high. The authors claim that NaCl and $BaCl_2$ are better promoters than comparable loadings of NH_4Cl and LiCl, indicating that the catalyst performance is partially due to the Na^+ and Ba^{2+} cations, not just the Cl^- anion. Promoter loadings either lower or higher than 3.8–4.5% NaCl gave catalysts with lower activity and selectivity.

Most of the reported work for epoxidation of propylene by heavily-modified, high weight loading Ag catalysts have been carried out by Gaffney and coworkers [48–53]. Catalyst compositions investigated by Gaffney include the following components and ranges of composition: 30–60% Ag, 0.5–3% K, 0.5–1% Cl, 0.5–2.5% Mo, 0.5–1% Re, 0.5–1% W, and balance $CaCO_3$. At these weight loadings of Ag and other moderators, it is not realistic to consider $CaCO_3$ as a support, since in some cases it is a minority component. Slurries of the components with powdered $CaCO_3$ are ball-milled, thoroughly mixing the $CaCO_3$ with the other components. After drying and calcining, the powder is pressed and shaped into granules or other preferred shapes. Gas phase feed compositions were typically 10% C_3H_6, 5% O_2, optionally 5–25% CO_2, and balance N_2 or other inert ballast gas, as well as 50–500 ppm organic halide, typically ethyl chloride, and 20–500 ppm NO. Most of the reactions were conducted at 250 °C at 30 psig (3 bar) pressure at a total GHSV of 1200 h^{-1}.

Gaffney showed that the complex recipe of catalyst components and gas phase promoters was required for both activity and selectivity to propylene oxide. Thus, a catalyst composed of 50 wt.% Ag and 50 wt.% $CaCO_3$ gave only 3% selectivity to propylene oxide, while a catalyst with Ag, K, and $CaCO_3$ without any organic chloride or NO feed promoter gave low conversion (<1%) and low selectivity (<3%). Co-feeding ethyl chloride and NO along with C_3H_6 and O_2 enhanced both conversion (up to 10%) and selectivity (up to 60%). The role of NO is poorly understood, although one hypothesis is that adding NO maintains a critical concentration of NO_3^- on the catalyst surface, although there is no explanation as to why NO_3^- is needed to enhance performance. The role of NO is further complicated by the observation that a catalyst containing Mo as a promoter has the same activity and selectivity with or without NO in the feed. The levels of ethyl chloride used with this process (typically about 200 ppm) are many times higher than the levels

currently used in either the epoxidation of ethylene or butadiene. In the latter cases, typical levels of organic chloride in the feed vary between 1 and 5 ppm [54,55]; levels higher than 5–10 ppm would result in continuous loss of activity for ethylene oxide and epoxybutene formation.

Even though the performance of this catalyst system is better than for the other propylene epoxidation options discussed above, the propylene oxide yield is still too low for commercial use. For a reported [49] activity of 3.2% conversion at 59% selectivity to propylene oxide using 2 cm^3 of catalyst at 30 psig and 245 °C, the calculated space time yield is 0.7 lbs propylene oxide/(l_{cat} h), which is at least an order of magnitude lower than ethylene oxide and epoxybutene production rates.

It is very difficult to determine any kind of catalyst surface structure–catalyst performance correlation with these catalysts, since surface compositions of these complex catalysts are so poorly defined. Not only are the concentrations of Ag, K, Cl much higher than commonly used to prepare ethylene oxide catalysts, the catalyst components are not deposited onto the $CaCO_3$ by wet impregnation or incipient wetness, but are actually thoroughly mixed with the $CaCO_3$ during preparation. Thus, it is not possible to determine whether the $CaCO_3$ functions primarily as a physical support, as a necessary component of the catalyst, or as a diluent for bulk silver.

If we consider these systems as a uniform mixture of silver and $CaCO_3$, the catalytic properties can be addressed in terms of the well-known ligand and ensemble effects of catalysis [56], whereby catalytic behavior is influenced by either the electronic properties of Ag sites interfaced with $CaCO_3$ (ligand effect), or by the sizes of contiguous arrays of Ag atoms that have different reactivity due to different size requirements (ensemble effect) for competing reactions. Ensemble effects are normally associated with metallic alloys, where the alloy surface can be theoretically diluted into ensembles of contiguous atoms of the catalytically-active component. It is not obvious that the type of atomic dilution inherent in ensemble theory is going to occur from physical mixing of a Ag salt and $CaCO_3$. Surface aggregates of Ag and $CaCO_3$ resulting from mixing should be much larger than the 5–20 atom aggregates typically considered to be relevant in catalysis. In fact, a correlation of Ag ensemble size for propylene oxidation over Ag–Au alloys has been carried out by Geneen et al. [57], who found that for Ag–Au alloy surfaces that were rich in gold (>70% Au at surface), C_3H_6 was selectively oxidized to acrolein (propenal); propylene oxide was produced only at trace amounts and did not change with the degree of gold alloying. The authors argued that while formation of propylene oxide did not exhibit an ensemble effect, the selective formation of acrolein indicated that small ensembles of Ag atoms were sufficiently large enough to effect the allylic oxidation of propylene to acrolein, but were too small to allow consecutive oxidation of acrolein to CO_2 and H_2O. Combustion required a larger number of Ag atoms to permit overlap of adsorbed acrolein with adjacent O-covered, Ag atoms.

The more logical possibility for the selective activity of the catalysts prepared by Gaffney is the existence of selective sites at the interface of the Ag and $CaCO_3$ portions of the catalyst. The need to further promote catalysts that are composed essentially of equal weights of Ag and $CaCO_3$ with high levels of K and Cl to obtain selective behavior may be to effectively poison the conventional Ag sites existing on the surface of the exposed silver surface, leaving only the interfacial Ag–$CaCO_3$ sites. If this is the case, one major goal of catalyst development and potential area for future research should be directed to increasing the concentration of active and selective sites, since current catalysts have activities too low for commercial utility. Regardless, this family of catalysts should be considered as one of the more promising new systems for selective epoxidation of propylene to propylene oxide. Since almost all information regarding the structure and performance of this novel system exists in patents, this is one area that could greatly benefit from a detailed study of better characterized catalysts to help elucidate the nature of the active and selective sites for propylene oxide formation.

3.2. Epoxidation of 1,3-butadiene

Monnier and coworkers [3,55,58–64] have demonstrated that it is possible to selectively epoxidize higher olefins to their corresponding epoxides using supported silver catalysts as long as the olefins do not contain reactive, allylic hydrogen atoms. Using an unpromoted Ag/α-Al_2O_3 catalyst, Monnier attempted

Table 3
Oxidation of olefins over unpromoted, 5% Ag/Al_2O_3 [a]

Reaction	Selectivity (%)	Conversion (%)
$CH_2{=}CH_2 + O_2$		12
EO	51	
CO_2	47	
$CH_2{=}CHCH_3 + O_2$		7
CO_2	92	
PO	0	
$CH_2{=}CHCHO$	8	
$CH_2{=}CHCH_2CH_3 + O_2$		8
CO_2	91	
BO	0	
$CH_2{=}CHCH{=}CH_2$	9	
$CH_3CH{=}CHCH_3 + O_2$		3.2
CO_2	98	
2-BO	0	
Other	2	
$CH_2{=}CHCH{=}CH_2 + O_2$		2.8
CO_2	25	
EpB™ oxirane	75	

[a] Reaction temperature = 250 °C and feedstream = helium/olefin/O_2 = 3:1:1.

the epoxidation of a series of olefins. The results, summarized in Table 3, indicated that while the observed selectivity to ethylene oxide was expected for an unpromoted catalyst, the selectivities to propylene oxide and butylene oxides were non-existent. In addition to small amounts of the selective allylic oxidation products (acrolein and butadiene in the cases of propylene and 1-butene, respectively), only CO_2 and H_2O were formed. However, the results for butadiene indicated it was possible to epoxidize this non-allylic olefin to 3,4-epoxy-1-butene, the mono-epoxide of butadiene. However, after only 2–3 h on line, catalytic activity declined from 2.8 to 0.8% conversion. Selectivity to epoxybutene also declined from 75 to 45%; non-selective products (and selectivities to these products) changed from essentially CO_2 (25%) to a mixture of CO_2 (4%), furan (11%), acrolein (24%), 2-butenal (16%), and a trace of 2,5-dihydrofuran (<1%) with the added reaction time. The three-pronged mechanistic scheme summarized in Fig. 2 was formally used to explain the source of all reaction products. The formation of epoxybutene is shown as 1,2-electrophilic addition of oxygen across either of the C=C double bonds. Acid-catalyzed isomerization of epoxybutene forms 2-butenal [65], or crotonaldehyde, which is thermodynamically-favored by 30.4 kcal/mol. Hydrogenolysis of the C_3–C_4 bond of an unspecified C_4-oxygenated intermediate provides a pathway for the formation of acrolein and formaldehyde, both of which were formed in approximate 1:1 molar ratios during the epoxidation reaction. Finally, the pathway for 1,4-addition of oxygen across the ends of butadiene initially forms 2,5-dihydrofuran, which undergoes facile allylic oxidation to give furan. The 1,4-addition route is the one favored by Roberts et al. [33] who analyzed by mass

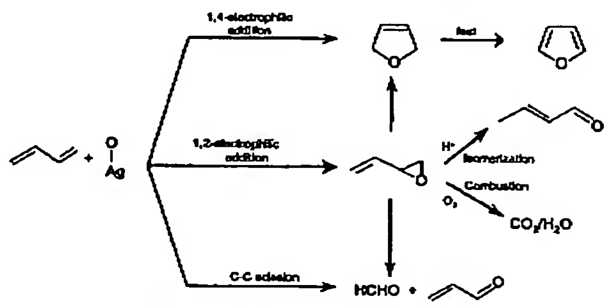


Fig. 2. General mechanistic scheme for C_4H_6 epoxidation.

spectroscopy the thermal desorption products of butadiene adsorbed on an oxygen-pre-covered Ag(1 1 0) surface and concluded the desorption products were primarily 2,5-dihydrofuran and furan. In later thermal desorption studies of 1-butene from Ag(1 1 0) surfaces, Roberts et al. [32] concluded that 1-butene was oxidatively dehydrogenated to form 1,3-butadiene, which then underwent 1,4-addition to initially form 2,5-dihydrofuran. In agreement with the above results, Schiøtt and Jørgensen [66] used extended Huckel calculations to determine the geometry of the interaction of butadiene on oxygen-covered Ag(1 1 0) planar surfaces and calculated that 1,4-addition of oxygen to form 2,5-dihydrofuran is thermodynamically-favored over 1,2-addition to form epoxybutene. The mechanism of Madix and calculations of Jørgensen did not provide any reasonable pathway for the formation of epoxybutene. Previous results for oxidation of butadiene using supported silver catalysts corroborate the results of Madix and Jørgensen. Parthasarathy and Hort [67] and Rao [68] evaluated 10% Ag/BPO_4 and 70% Ag/MoO_3, respectively, as catalysts for butadiene oxidation and found that, in both cases, the preferred oxidation product was furan which was formed by oxidation of 2,5-dihydrofuran as the primary product. Neither catalyst, however, was very active or selective for furan formation.

The difficulty with the above results is that the formation of epoxybutene is not satisfactorily explained. Thermodynamically, the isomerization of 2,5-dihydrofuran to form epoxybutene is unfavored by 19.5 kcal/mol. To determine which, if any, of the reaction pathways in Fig. 2 was dominant during butadiene epoxidation, realistic concentrations of each of the reaction intermediates in Fig. 2 were sequentially added to the reactor feedstream during the epoxidation reaction. The results, which are shown in Table 4, indicate that (a) furan does not undergo further reaction, (b) 2,5-dihydrofuran is selectively oxidized to furan, (c) crotonaldehyde, or 2-butenal, is only slightly oxidized to CO_2/H_2O, and (d) epoxybutene is not only converted to furan (via 2,5-dihydrofuran), acrolein, crotonaldehyde, and CO_2, only 55% of the epoxybutene which was added could be accounted for. Thus, epoxybutene was the only reaction intermediate that could account for all observed reaction products (and in the appropriate ratios) during butadiene epoxidation. Further, the net rate of epoxybutene formation was greatly suppressed during the period of time that epoxybutene was externally added to the reactor feedstream. The activity was slowly restored when epoxybutene was removed from the feed, indicating a strong kinetic inhibition by epoxybutene for the formation of epoxybutene. The strongly-bound epoxybutene was also the reason for poor accountability of epoxybutene when it was added to the feedstream.

The results from co-feeding of epoxybutene suggested that all reaction products could be satisfactorily explained by the direct 1,2-addition of oxygen to adsorbed butadiene to initially form epoxybutene. The strong adsorption of epoxybutene resulted in rearrangement to form 2,5-dihydrofuran and furan as well the hydrogenolysis products, acrolein and formaldehyde; the strong adsorption also explained the kinetic inhibition effect of epoxybutene. Although the preference for 1,2-addition of oxygen to one of the localized C=C double bonds of butadiene is not predicted by the thermal desorption work of Madix,

Table 4
Addition of reaction products to feedstream during butadiene epoxidation

	Feed additive			
	Furan	Crotonaldehyde	2,5-DHF	Epoxybutene
Furan	N/A	0	75	4
Acrolein	0	0	0	4
2,5-DHF	0	0	N/A	0
Epoxybutene	0	0	0	N/A
Crotonaldehyde	0	N/A	6	25
CO_2	0	4	16	14
Conversion of additive (%)	0	4	24	46
Accountability of additive (%)	100	100	97	55

one explination for Madix' results is that the strong adsorption of epoxybutene on the unpromoted (1 1 0) silver surface permitted rearrangement to the more thermodynamically-stable 2,5-dihydrofuran, which resembles 1,4-addition. The actual geometry of the reaction intermediate during 1,2-addition is not known, although the intermediate is likely to be similar to that proposed during epoxidation of ethylene, which is considered to be concerted addition of an adsorbed oxygen atom across both carbon atoms of a C=C double bond. Alternatively, Bartesa and coworkers [69,70] have used a combination of density functional theory (DFT) calculations and high resolution electron energy loss spectroscopy (HREELS) to conclude that all silver-catalyzed olefin epoxidation reactions proceed through oxametallacycle intermediates. For epoxybutene formation, the terminal carbon atom of one of the C=C double bonds would be bonded to an oxygen atom which is adsorbed on a Ag site; the adjacent internal carbon would also be bonded, in this case to a Ag atom, giving a five-membered oxametallacycle. According to Medlin and Bartesa, ring closure and desorption of this intermediate forms epoxybutene. This somewhat controversial intermediate and mechanism for olefin epoxide formation has re-initiated interest in the mechanism of olefin epoxidation.

Promotion of the unsupported catalyst by CsCl greatly improved activity, selectivity to epoxybutene, and stability. Promotion by 1000 ppm Cs (added as CsCl) increased conversion from 0.8 to 12.0% and selectivity form 45 to 92%. Catalyst lifetime increased from several hours to greater than the length of testing (>24 h). Measurement of the apparent activation energy for epoxybutene formation showed that E_{app} was lowered from 40.7 before promotion to 26.4 kcal/mol after promotion by CsCl. A different approach has been used by Boeck and coworkers [71,72] to maintain activity for silver catalysts used for butadiene epoxidation. The authors report that steam at concentrations between 6 and 80 mol% can be added to the reactor feed to lower the rate of fouling and, thus, increase lifetime. While lifetime is somewhat extended (catalyst must still be periodically regenerated by calcination), catalyst activity and selectivity remain unacceptably low, due to the inherent kinetic inhibition effect of epoxybutene. The reported space time yield at 220 °C and a GHSV of 250 h^{-1} was 0.5 lbs epoxybutene/(h ft^3) catalyst at

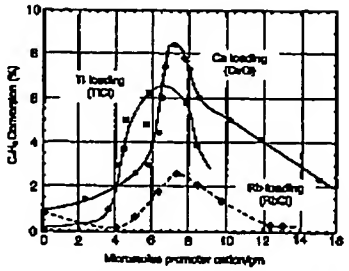


Fig. 3. Promoter loading vs. catalyst performance. Reaction temperature = 210 °C, feed composition is n-C_4H_{10}/C_4H_6/O_2 = 4:1:1 at GHSV = 5400 h^{-1}. Selectivities to epoxybutene at optimum loading: CsCl = 94.3%, RbCl = 93.5% and TlCl = 90.0%.

a selectivity of 82–84%, which is much lower than the results reported by Monnier et al. The long-term effects of water in the presence of epoxybutene at reaction temperatures are also questionable since it is known that epoxybutene is hydrolyzed by water to form 3-buten-1,2-diol [73], which has physical and chemical properties that might lead to even more deactivation than epoxybutene alone.

The curves in Fig. 3 show that promotion by CsCl gives a maximum activity at approximately 950 ppm Cs, or 7.0 μmol Cs/g_{cat}, for this family of supported silver catalysts. Likewise, promotion by RbCl and TlCl also indicate that loadings of approximately 7–8 μmol Rb and Tl/g_{cat} result in maximum activity for epoxybutene formation. Catalysts promoted by KCl over the same concentration range did not exhibit similar enhancements in either activity or selectivity; performance was essentially the same as for unpromoted catalysts. Reaction conditions for the promoted 12 wt.% Ag/α-Al_2O_3 catalyst in all cases were 1 bar pressure and 210 °C using a feed composition of $He/C_4H_6/O_2$ = 4:1:1 at a GHSV of 5400 h^{-1}. It is interesting to note that optimum promoter loadings of Rb, Cs, and Tl all occur at similar molar loading levels, suggesting a specific and common type of interaction (rather than random deposition of promoter) of the promoter with the silver surface. That the interaction

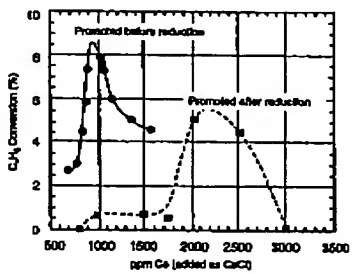


Fig. 4. Effect of Ag salt reduction on promoter efficiency. Reaction temperature = 210 °C, feed composition is n-$C_4H_{10}/C_4H_6/O_2$ = 4:1:1 at GHSV = 5400 h^{-1}.

of the promoter salts occurs with the silver surface, and not the α-Al_2O_3 support, can be inferred from the curves in Fig. 4 for two series of catalysts which have been promoted at different stages of preparation. The sample promoted before reduction of the Ag salt precursor shows a sharp maximum at approximately 950 ppm Cs, while the sample promoted by Cs after reduction of the silver salt to Ag/α-Al_2O_3 yields a broad maximum between 2000 and 2500 ppm Cs. The location of the optimum promoter loading at higher Cs loadings suggests that the Cs is deposited on both the Ag and α-Al_2O_3 surfaces of the catalyst, while in the case of co-impregnation of the Ag and Cs salt, the Cs is targeted much more effectively onto the Ag surface. Likewise, the interaction of the Cs promoter appears to be more effective when deposited before reduction of the Ag salt, since butadiene conversions are substantially higher (8% conversion versus 5.5% conversion, respectively), when the promoter is added before reduction.

Selected physical and electronic properties of different promoter cations are summarized in Table 5. The Cs^+, Rb^+, and Tl^+ salts that have shown positive promoter effects for epoxybutene formation have cations that are large and highly polarizable [74]. In fact, the ionic radii and the values of the Pauling polarizabilities of Cs^+, Rb^+, and Tl^+ are the largest of any of the naturally-occurring elements. Thus, the successful promoters are large and highly polarizable ions under reaction conditions. As stated above, catalysts promoted by K^+ salts are not active for epoxybutene formation, suggesting that size alone is not the critical factor in determining promoter efficiency. If promoters function merely by blocking, or neutralizing, non-selective sites, then K should show some promoter effect for epoxybutene formation, based on size and reactivity of alkali metals. Polarizability, or the measure of an ion's ability to deform its electronic core to external electric fields, may be a more important factor in determining promoter efficiency than size alone.

Table 5
Properties of promoter cations for butadiene epoxidation

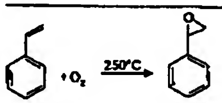
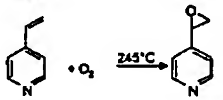
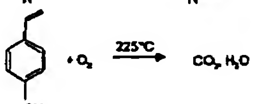
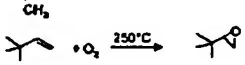
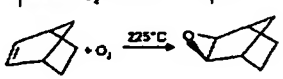
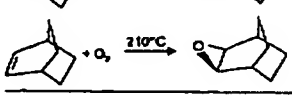
Cation (+1)	Ionic radius (Å)	Charge/surface	Polarizability
Lithium	0.78	0.130	0.03
Sodium	0.98	0.085	0.03
Potassium	1.33	0.045	1.1K
Rubidium	1.49	0.035	1.9K
Cesium	1.65	0.030	2.9K
Thallium	1.40	0.040	4.3K
Silver	1.26	-	-

For catalysts optimized for epoxybutene production, the 900–1000 ppm level of Cs loading is substantially higher than the 200–300 ppm Cs loadings typically used for ethylene oxide formation [75]. In fact, a catalyst optimized for epoxybutene formation is essentially inactive for ethylene oxide, while a catalyst optimized for ethylene oxide formation is inactive for epoxybutene [3]. These results clearly indicate the impact of differences in kinetics on promoter requirements for otherwise similar reactions. For epoxybutene formation, the rate limiting step involves desorption of epoxybutene [3], while for ethylene oxide formation, the rate determining step is considered to be the surface reaction between adsorbed ethylene and adsorbed oxygen [54]. However, for both reactions, the active oxygen used to form the epoxide is atomic oxygen [76,77], and not molecular oxygen [54]. Application of the 6/7 rule that has been used to rationalize the role of molecular oxygen in ethylene epoxidation would limit the selectivity of epoxybutene to 11/12, or <91.7%. Selectivity values >91.7%, and as high as 94–96%, have been reported in Monnier and coworkers [58–64] work.

3.3. Epoxidation of higher olefins

In addition to butadiene, Monnier has reported the selective epoxidation of higher non-allylic olefins such as styrene [78] and 3,3-dimethyl-1-butene [58] and hindered allylic olefins, such as norbornene [79], using Cs- and Rb-promoted, silver catalysts; results are summarized in Table 6. The data for the epoxidation of styrene and 4-vinylpyridine show that these catalysts are both active and selective for the formation of their respective epoxides and corroborate earlier work by Blum [80] for supported silver catalysts and by Hawker et al. [76] for temperature-programmed reaction spectroscopy of styrene adsorbed on oxygen-covered Ag(1 1 1) single crystal surfaces. However, in the examples of Blum, weight loadings of Na, K, Li, and Cs between 7000 and 60,000 ppm/g_{cat} were used to promote the supported silver catalysts for the epoxidation of styrene. Thus, a catalyst having a composition of 39,800 ppm K (3.98%) and 16.8% Ag supported on α-Al_2O_3 exposed to a stream of 70% O_2, 7% styrene, and 23% N_2 at 284 °C gave 13% conversion of styrene and a selectivity to styrene oxide of 85% at a GHSV of 1200 h^{-1}. Conversely, the promoter loadings reported by Monnier ranged from 435 to 2620 ppm for Rb promoted compositions and 345–1350 ppm for Cs-promoted, silver catalysts. For both families of promoted catalysts, catalytic activities passed through a maximum at the intermediate promoter loadings of Rb and Cs. A catalyst with a composition of 1000 ppm $CsNO_3$ (680 ppm Cs) and 15% Ag supported on α-Al_2O_3 that was exposed to a stream of 10% O_2, 2% styrene, and 88% He at 3600 h^{-1} space velocity and 250 °C gave 66% conversion of styrene at a selectivity to styrene oxide of 95%. It is not obvious why the catalysts evaluated by Blum contained much higher levels of promoter salts; no data were included for catalysts with lower promoter loadings.

Table 6
Epoxidation of other olefins using CsCl-promoted, Ag/Al_2O_3 catalysts

Reaction	Molar selectivity (%)	Conversion (%)
	95	19
	93	21
	0	100
	95	1.5
	92	43
	36	4

The results in Table 6 indicate that the presence of the *para*-CH_3 group in 4-vinyltoluene results in combustion of this olefin to CO_2/H_2O. While the $-CH_3$ group is not allylic to the vinyl group, it is both allylic and benzylic to the aromatic ring and is very reactive towards C–H bond breaking during oxidation. This reactivity and subsequent combustion of 4-vinyltoluene prevents formation of the epoxide. *Tert*-butyl ethylene, another non-allylic olefin in Table 6, is also very selectively epoxidized; however, the bulky *tert*-butyl group lowers reactivity of this olefin.

The results for epoxidation of norbornene in Table 6 indicates that Cs-promoted, silver catalysts also selectively epoxidize allylic olefins to their corresponding epoxides, as long as the allylic C–H groups are kinetically non-reactive. The results for norbornene agree well with the temperature-programmed reaction spectroscopy results of Roberts and Madix [77], who observed that norbornene epoxide desorbed at approximately 310°K from a Ag(1 1 0) surface which had been pre-adsorbed with norbornene and atomic oxygen. In a related study, Cant et al. [81] reported that during continuous oxidation of norbornene by molecular oxygen over an unpromoted silver sponge catalyst only benzene was formed as the oxidation product. The authors concluded that norbornene oxide was not an intermediate during formation of benzene. Data from Monnier and Muehlbauer [79] for unpromoted silver catalysts confirm that only trace amounts of norbornene oxide are produced by unpromoted catalysts, but that Cs-promoted, silver catalysts are very active and selective for epoxide formation. The results of Cant are consistent with norbornene epoxide being the primary product, but that the strongly-bound norbornene epoxide undergoes hydrogenolysis and oxidative dehydrogenation to form benzene, in a manner analogous to acrolein and furan formation during epoxidation of butadiene over unpromoted silver catalysts.

The importance of ensuring that olefins contain no reactive, allylic C–H bonds is seen by comparing the selectivity differences between epoxidation of norbornene and bicyclo[2.2.2]oct-2-ene. Epoxidation of bicyclo[2.2.2]oct-2-ene is only 36% selective to the desired epoxide. The addition of the additional $-CH_2$ group in the bridging position results in a dramatic decrease in selectivity, presumably because the less puckered geometry of bicyclo[2.2.2]oct-2-ene makes the allylic hydrogen more accessible and reactive with the Ag–O surface. It is not possible to state whether the more favorable C–H bond angle of the allylic C–H bond, or the lower strain energy of the allylic structure (after C–H bond rupture), are responsible for the lower observed selectivity to the olefin epoxide. However, comparison of these two bicyclic olefins toward olefin epoxidation does underscore the importance of having no reactive, allylic C–H bonds for selective epoxidation to occur using supported silver catalysts.

4. Conclusions

Recent developments in olefin epoxidation have indicated it is possible to epoxidize higher olefins directly by using molecular oxygen, or indirectly, by using molecular oxygen to generate an active and selective oxidant in situ during reaction. The commonly-practiced methodology of systematic and minor modifications of pre-existing catalysts and technology, in this case, the epoxidation of ethylene, have not been successful in advancing olefin epoxidation. In each instance of successful epoxidation of higher olefins, discontinuous changes from traditional approaches have been required. One novel approach has recognized that while it is known that H_2O_2 is active and selective for epoxidation, the high cost of H_2O_2 has prevented its use as a practical oxidant. However, the in situ generation of H_2O_2 from H_2 and O_2 under olefin epoxidation reaction conditions is a potentially inexpensive way to combine H_2O_2 with conventional olefin epoxidation catalysts, such as TS-1 and TiO_2. These bifunctional catalysts have combined new catalyst components that generate H_2O_2 in situ with the functional component that activates H_2O_2 for olefin epoxidation. Generation of H_2O_2 from H_2 and O_2 is a difficult research problem, especially in the presence of an olefin. Not only one must be concerned with selective use of H_2 and O_2 to generate H_2O_2, and not H_2O, the competing hydrogenation reaction of the

olefin to form the corresponding paraffin is another facile reaction that must be suppressed. Current bifunctional catalysts use either a combination of noble metal components, such as Pt-Pd, to generate H_2O_2, or the unique properties of small supported gold particles to generate H_2O_2. In both cases, the primary limitations of these bifunctional catalysts are the low rates of H_2O_2 formation (and subsequent low rates of olefin epoxide formation) and the non-selective consumption of H_2 (which generates H_2O) and olefins (which generate paraffins). Other problems include stability of these bifunctional compositions under reaction conditions and the potential flammability hazards associated with handling gas mixtures containing both H_2 and O_2.

Another novel approach employs silver-based methodology, but in much different combinations of weight loadings of silver, promoters, and support than typically used for ethylene oxide catalysts. These catalysts, which have been used for propylene epoxidation, have much higher silver, alkali metal, alkaline earth, and chlorine loadings than the analogs used for ethylene oxide formation, and are quite different in terms of their physical and chemical properties. The silver and promoters are not supported in these compositions, but are actually uniformly mixed with the carrier, typically alkaline earth carbonates, such as $CaCO_3$. In some compositions, the modified silver composition is even unsupported. While the selectivities to propylene oxide are considerably higher than with conventional silver catalysts, selectivities and rates of olefin epoxide are still too low for commercial application. However, the improved performance of these catalysts is noteworthy. Since almost all information regarding the structure and performance of this novel system exists in patents, this is one area that could greatly benefit from a detailed study of better characterized catalysts to help elucidate the nature of the active and selective sites for propylene oxide formation.

Yet another approach has been to use silver-based catalysts for the selective epoxidation of non-allylic olefins, recognizing that the reactivity of allylic hydrogen atoms makes the use of conventional silver-based catalysts unrealistic. Although the kinetic slow step for epoxidation of higher, non-allylic olefins is different from that for ethylene epoxidation, changes in the promoter loading levels have permitted the selective epoxidation of olefins such as 1,3-butadiene, styrene, and kinetically-hindered olefins, such as norbornene. This has led to the commercialization of butadiene epoxidation to form epoxybutene, the first olefin epoxide to be commercially-produced since ethylene oxide was commercialized.

In summary, direct olefin epoxidation by molecular oxygen is an extremely important class of catalytic reaction. The recent examples of progress discussed in this article indicate that there is much left to exploit in direct epoxidation of higher olefins. Many of the compositional and structural features of these novel catalysts are poorly understood. Likewise, many of the kinetic features and reaction intermediates of higher olefin epoxidation remain to be elucidated. These are areas of catalytic research that, if successful, would have tremendous implications on growth of the chemical process industry at a time when many believe that the chemical industry is mature. Olefin epoxides as a class of chemical compound are arguably one of the most versatile families of chemicals produced today.

Acknowledgements

I would like to thank management at Eastman Chemical Company for permission to publish this paper. I am also grateful for the assistance of Ms. Suzanne Monnier for careful reading of this manuscript and the efforts of Ms. Libby Cradic and Ms. Valecia Fillnow in preparing the final format of this manuscript and accompanying figures and tables.

References

[1] Chemical and Engineering News, 28 June 1999, p. 32.
[2] Chemical and Engineering News, 21 August 1995, p. 7.
[3] J.R. Monnier, Stud. Surf. Sci. Catal. 110 (1997) 135.
[4] J. A. Dean, Lange's Handbook of Chemistry, McGraw-Hill, New York, 1992, p. 4.25.
[5] G.I. Mackay, M.H. Lien, A.C. Hopkinson, D.K. Bohme, Can. J. Chem. 56 (1978) 131.
[6] S.-H. Wang, SRI Report no. 2B, 1994, p. 2-1.
[7] M. Tamarasso, G. Perego, B. Notari, US Patent 4,410,501 (1983) to Snamprogetti S.p.A.
[8] B. Notari, Stud. Surf. Sci. Catal. 67 (1991) 243.
[9] M.G. Clerici, G. Bellussi, U. Romano, J. Catal. 129 (1991) 159.
[10] R.A. Budnik, J.K. Kochi, J. Org. Chem. 41 (1976) 1384.
[11] J. Bouchard, M. De Pauw, J. Catal. 14 (1969) 134.

[12] T. Mukaiyama, T. Takai, T. Yamada, O. Rhode, Chem. Lett. (1990) 1661.
[13] D. Y. Waddan, D. Williams, US Patent 4,390,738 (1983) to Imperial Chemical Industries, PLC.
[14] R.A. Grey, US Patent 5,670,674 (1997) to ARCO Chemical Technology, L.P.
[15] I. Yamanaka, K. Nakagaki, T. Akimoto, K. Otsuka, Chem. Lett. (1994) 1717.
[16] K.A. Jørgensen, Chem Rev. 89 (1989) 431.
[17] B.T. Pennington, US Patent 4,785,123 (1988) to Olin Corporation.
[18] B.T. Pennington, M.C. Fullington, US Patent 4,943,643 (1990) to Olin Corporation.
[19] J.L. Meyer, B.T. Pennington, US Patent 4,992,567 (1991) to Olin Corporation.
[20] R. Meiers, U. Dingerdissen, W.F. Hölderich, J. Catal. 176 (1998) 376.
[21] R. Meiers, W.F. Hölderich, Catal. Lett. 59 (1999) 161.
[22] M.G. Clerici, P. Ingallina, Catal. Today 41 (1998) 351.
[23] T. Hayashi, K. Tanaka, M. Haruta, J. Catal. 178 (1998) 566.
[24] T. Hayashi, L.B. Han, S. Tsubota, M. Haruta, Ind. Eng. Chem. Res. 34 (1995) 2298.
[25] B.S. Uphade, M. Okumura, S. Tsubota, M. Haruta, Appl. Cat. A: Gen. 190 (2000) 43.
[26] Y.A. Kalvachev, T. Hayashi, E. Tsubota, M. Haruta, J. Catal. 186 (1999) 228.
[27] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. 115 (1989) 301.
[28] S.D. Lin, M. Bollinger, M.A. Vannice, Catal. Lett. 17 (1993) 245.
[29] G.C. Bond, Catal. Rev.-Sci. Eng. 41 (1999) 319.
[30] P.H. Kasai, J. Am. Chem. Soc. 106 (1984) 3069.
[31] R.B. Grant, R.M. Lambert, J. Catal. 92 (1985) 364.
[32] J.T. Roberts, A.J. Capote, R.J. Madix, Surf. Sci. 253 (1991) 13.
[33] J.T. Roberts, A.J. Capote, R.J. Madix, J. Am. Chem. Soc. 113 (1991) 9848.
[34] T.A. Nijhuis, B.J. Huizinga, M. Makkee, J.A. Moulijn, Ind. Eng. Chem. Res. 38 (1999) 884.
[35] J.R. Anderson, Structure of Metallic Catalysts, Academic Press, New York, 1975, pp. 290–300.
[36] M. Weisbeck, E. Dorf, G. Wegener, C. Schild, B. Lücke, H. Dilcher, U. Schelke, WO Appl. 99/40077 (1999) to Bayer Chemical Company.
[37] R.P. Schulz, U. Dingerdissen, H. Oracek, W. Maier, German Patent 19754303 (1999) to Hoechst A.-G.
[38] M. Haruta, K.L. Angelov, T. Tsubota, T. Hayashi, Japan Patent 11076820 (1999) to Nippon Shokubai Kagaku Kogyo Co., Ltd.
[39] M. Haruta, K. J. Angelov, T. Tsubota, T. Hirashi, M. Wada, Japan Patent 11128743 (1999) to Nippon Shokubai Kagaku Kogyo Co., Ltd.
[40] R.G. Bowman, J.L. Womack, H.W. Clark, WO Appl. 98/00413 (1998) to Dow Chemical Company.
[41] R.G. Bowman, J.J. Maj, H.W. Clark, G.E. Hartwell, J.L. Womack, S.R. Bare, WO Appl. 98/00414 (1998) to Dow Chemical Company.
[42] H.J. Clark, J.J. Maj, R.G. Bowman, S.R. Bare, G.E. Hartwell, WO Appl. 98/00415 (1998) to Dow Chemical Company.
[43] M.A. Barteau, R.J. Madix, J. Am. Chem. Soc. 105 (1983) 344.
[44] A.J. Kolombos, C.C. McCain, British Patent 1,327,497 (1973) to British Petroleum Chemicals Limited.
[45] B.M. Thorsteinson, Canadian Patent 1,286,772 (1991) to Union Carbide Corporation.
[46] R.G. Bowman, US Patent 4,845,253 (1989) to Dow Chemical Company.
[47] G. Lu, X. Zuo, Catal. Lett. 58 (1999) 67.
[48] R. Pitchai, A.P. Kahn, A.M. Gaffney, US Patent 5,625,084 (1997) to ARCO Chemical Technology, L.P.
[49] R. Pitchai, A.P. Kahn, A.M. Gaffney, US Patent 5,686,380 (1997) to ARCO Chemical Technology, L.P.
[50] A.M. Gaffney, C.A. Jones, R. Pitchai, A.P. Kahn, US Patent 5,698,719 (1997) to ARCO Chemical Technology, L.P.
[51] A.M. Gaffney, A.P. Kahn, R. Pitchai, US Patent 5,703,254 (1997) to ARCO Chemical Technology, L.P.
[52] B. Cooker, A.M. Gaffney, J.D. Jewson, A.P. Kahn, R. Pitchai, US Patent 5,770,746 (1998) to ARCO Chemical Technology, L.P.
[53] B. Cooker, A.M. Gaffney, J.D. Jewson, A.P. Kahn, W.H. Onimus, US Patent 5,780,657 (1998) to ARCO Chemical Technology, L.P.
[54] W.M.H. Sachtler, C. Backx, R.A. Van Santen, Catal. Rev.-Sci. Eng. 23 (1981) 127.
[55] J.R. Monnier, P.J. Muehlbauer, US Patent 4950,773 (1990) to Eastman Chemical Company.
[56] W.M.H. Sachtler, R.A. Van Santen, J. Catal. 26 (1977) 69.
[57] P.V. Geenen, H.J. Boss, G.T. Pott, J. Catal. 77 (1982) 499.
[58] J.R. Monnier, P.J. Muehlbauer, US Patent 4897,498 (1990) to Eastman Chemical Company.
[59] J.R. Monnier, P.J. Muehlbauer, US Patent 5138,077 (1992) to Eastman Chemical Company.
[60] J.R. Monnier, P.J. Muehlbauer, US Patent 5081,096 (1992) to Eastman Chemical Company.
[61] J.L. Stavinoha, J.R. Monnier, D.M. Hitch, T.R. Nolen, G.L. Oltean, US Patent 5,362,890 (1994) to Eastman Chemical Company.
[62] G.L. Oltean, J.R. Monnier, US Patent 5,905,942 (1999) to Eastman Chemical Company.
[63] S.D. Barnicki, J.R. Monnier, K.T. Peters, US Patent 5,945,550 (1999) to Eastman Chemical Company.
[64] S.D. Barnicki, J.R. Monnier, US Patent 6,011,163 (2000) to Eastman Chemical Company.
[65] R.J. Crawford, S.B. Lutener, R.D. Cockcroft, Can. J. Chem. 54 (1976) 3364.
[66] D. Schloss, K.A. Jørgensen, J. Phys. Chem. 97 (1993) 10738.
[67] R. Parthasarathy, E.V. Hort, US Patent 4,293,444 (1981) to GAF Corporation.
[68] V.N.M. Rao, US Patent 4,474,997 (1984) to E. I. DuPont de Nemours and Company.
[69] J.W. Medlin, M.A. Barteau, Oxametallacycle intermediates in epoxide chemistry: a combined theoretical/experimental approach, in: Proceedings of the Annual Meeting of the American Institute of Chemical Engineers, November 1999, Presentation no. 235.

[70] J.W. Medlin, M. Mavrikakis, M.A. Barteau, J. Phys. Chem. B 103 (1999) 11169.

[71] S. Boeck, K. Herzog, R. Fischer, H. Vogel, Martin Fischer, US Patent 5,618,954 (1997) to BASF Aktiengesellschaft.

[72] S. Boeck, K. Herzog, R. Fischer, H. Vogel, Martin Fischer, US Patent 5,905,161 (1999) to BASF Aktiengesellschaft.

[73] P.B. Mackenzie, J.B. Kanel, S.N. Falling, US Patent 5,856,591 (1999) to Chemical Company.

[74] B.E. Douglas, D.H. McDaniel, Concepts and Models of Inorganic Chemistry, Blaisdell, Waltham, MA, 1965, pp. 102-113, 345-348.

[75] A.M. Lauritzen, US Patent 4,761,394 (1988) to Shell Oil Company.

[76] S. Hawker, C. Mukoid, J.S. Badyal, R.M. Lambert, Surf. Sci. 219 (1989) L615.

[77] J.T. Roberts, R.J. Madix, J. Am. Chem. Soc. 110 (1988) 8540.

[78] J.R. Monnier, P.J. Muehlbauer, US Patent 5,145,968 (1992) to Eastman Chemical Company.

[79] J.R. Monnier, P.J. Muehlbauer, WO Appl. 90/11279 (1990) to Eastman Chemical Company.

[80] P.R. Blum, US Patent 4,894,467 (1990) to The Standard Oil Company.

[81] N.W. Cant, E.M. Kennedy, N.J. Ossipoff, Catal. Lett. 9 (1991) 133.